

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
2 August 2001 (02.08.2001)

PCT

(10) International Publication Number
WO 01/55227 A2

(51) International Patent Classification⁷:

C08F

(74) Agent: G. E. EHRLICH (1995) LTD.; 28 Bezalel Street,
52 521 Ramat Gan (IL).

(21) International Application Number: PCT/IL01/00073

(22) International Filing Date: 25 January 2001 (25.01.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/492,033 27 January 2000 (27.01.2000) US

(71) Applicant (for all designated States except US): TECHNION RESEARCH AND DEVELOPMENT FOUNDATION LTD. [IL/IL]; Gutwirth Science Park, Technion City, 32 000 Haifa (IL).

(72) Inventors; and

(75) Inventors/Applicants (for US only): EISEN, Moris [IL/IL]; 68 Hashkdim Street, 34 601 Tivon (IL). VOLKIS, Victoria [IL/IL]; Neve Sha'anana, 61 Netivey Chen Street, 32 688 Haifa (IL). SHMULINSON, Michael [IL/IL]; Ramat Almogi, 9 Hasachlav Street, 34 790 Haifa (IL). AVERBUIJ, Claudia [IL/IL]; 1 Einav Street, 21 970 Carmiel (IL). TISH, Edith [IL/IL]; 16 Arie Street, 78 701 Ashkelon (IL).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



A2

(54) Title: PROCESS FOR THE PRODUCTION OF STEREOREGULAR POLYMERS AND ELASTOMERS OF ALPHA-OLEFINS AND CERTAIN NOVEL CATALYSTS THEREFOR

(57) Abstract: A process for the polymerization of one or more alpha-olefins having at least 3 carbon atoms, which comprises contacting the monomer or monomers in a polar or non-polar solvent under polymerization conditions with a homogeneous catalyst system including (a) a cationic form of a racemic mixture of a chiral octahedral transition metal complex or of a non chiral octahedral transition metal complex, comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands and having C₁, C₂, or C₃ symmetry; and (b) an anion of a Lewis acid or a Brönsted acid; and adjusting the pressure so as to obtain either a highly stereoregular polymer or copolymer or an elastomer.

WO 01/55227

BEST AVAILABLE COPY

PROCESS FOR THE PRODUCTION OF STEREOREGULAR POLYMERS
AND ELASTOMERS OF ALPHA-OLEFINS AND CERTAIN NOVEL
CATALYSTS THEREFOR

5 FIELD AND BACKGROUND OF THE INVENTION

The present invention relates to (i) the use of octahedral transition metal complexes as precatalysts for the polymerization of alpha-olefins; (ii) the use of homogeneous catalyst systems comprising these complexes and (iii) a novel 10 class of such complexes. More particularly, the invention relates to the use of cationic chiral, racemic or non-chiral catalysts of the above-mentioned type for the polymerization of alpha-olefins to produce highly stereoregular polymers or poly alpha-olefin elastomers.

The polymerization of alpha-olefins with Ziegler-Natta catalysts is well-known in the chemical industry and it is used to a large extent. The various 15 polymers that are derived from the polymerization of such olefins show differences in their chemical and physical properties, as a result of differences in molecular structure and molecular weights. Polymers of alpha-olefins having three or more carbon atoms as the monomeric unit will have pendant 20 hydrocarbyl groups attached to the polymer backbone chain. The arrangement of these hydrocarbyl groups along the polymer backbone will determine, to a large extent, the physical properties of a particular polymer. For example, strong polymers tend to be stereochemically regular meaning that the adjacent pendant hydrocarbyl groups reside on the same side of the polymer backbone.

25 Three major types of stereoregularity, or tacticity have been

characterized: atactic, isotactic and syndiotactic configurations. Atactic polyolefins are those wherein the pendant hydrocarbyl groups have no regular order in space with reference to the backbone and to other pendant groups. These are amorphous materials and are generally unsuitable for applications 5 where high strength is required. Isotactic polyolefins are those wherein the pendant hydrocarbyl groups are ordered in space on the same side or plane of the polymer backbone chain. Polyolefins that are highly isotactic exhibit a high degree of crystallinity and high melting points, and accordingly are particularly suited to high strength applications.

10 The degree of stereoregularity may be determined from the pentad analysis using carbon-NMR techniques. A purely isotactic polyolefin will have a degree of crystallinity (mmmm) value of close to 100, whereas atactic poly alpha-olefins will have a theoretical statistical value of 6.5.

Syndiotactic polyolefins are those wherein the pendant hydrocarbyl 15 groups of the polymer backbone alternate sequentially from one side or plane to the opposite side or plane relative to the polymer backbone. Although syndiotactic polymers, as compared with the corresponding isotactic polymers, are characterized by lower melting points, they are generally suitable for high strength applications, provided that their molecular weight exceeds 100,000 20 daltons.

Another category of high polymers with special stereosequencing is elastic polymers, or elastomers. As taught by Textbook of Polymer Science

(edited by Fred W. Billmeyer, Jr., 3rd edition, Wiley Interscience: New York, 1984), page 507, the unique properties of elastomers include their ability to stretch and retract rapidly. Elastomers exhibit high strength and modulus while stretched, and recover fully on release of the stress. To obtain these properties, 5 certain requirements are placed upon the molecular structure of the compounds: they must be high polymers, be above their glass transition temperatures, be amorphous in the unstretched state, but preferably develop crystallinity on stretching, and contain a network of crosslinks to restrain gross mobility of the chains.

10 In addition to the above-mentioned form of elastic polymers, polymers that contain crystalline areas (domains) and amorphous areas also exhibit elastomeric properties. This can be achieved in different ways, leading to (at least) two different microstructures, both of which are germane to the instant invention:

15 (a) a polymer containing domains of stereoregular and atactic sections, consecutively arranged in each polymer chain; and

(b) a stereoregular polymer in which the inclusion of numerous stereoregular mistakes provides the material with atactic parts.

20 The polymer described in (b) has elastomeric properties because the crystalline, stereoregular parts of the chains form lamellae, and the mistakes, incorporated into the otherwise stereoregular sequences, and when present in sufficient quantity, form the amorphous domains that provide the material with

elastomeric properties.

One of the most important parameters to measure the elasticity is the modulus (for elongation of 300-400 %). For example, natural rubber and SBR polymers have a modulus of 2500 psi; neoprene, which is not very elastic, has a 5 modulus of about 1000 psi; isotactic polypropylene has a modulus of 91 psi.

Conventional titanium and zirconium based Ziegler-Natta catalysts for the preparation of isotactic polymers are well known in the art. The systems are, however, limited in terms of molecular weight, molecular weight distribution and tacticity control. Additional methods of producing isotactic 10 polymers from an alumoxane cocatalyzed metallocene were reported by Ewen, J. Am. Chem. Soc., 106, 6355 (1984) and Kaminsky et al., Angew. Chem. Int. Ed. Eng., 24, 507 (1985).

The use of cocatalyzed catalyst systems for the production of highly crystalline polyolefins is disclosed in U.S. Pat. No. 5,318,935. The catalyst 15 systems described therein comprise a complex formed upon admixture of the amido group IVb transition metal component with an alumoxane component.

According to a recent review (M. S. Eisen et al., J. Organometallic Chem., 503, 307 (1995)), a series of bis(trimethylsilyl)benzamidinate zirconium dichlorides are described as active catalysts for ethylene polymerization. As 20 taught therein, the polymerization activity increases drastically with increasing pressure. However, these catalyst systems are generally characterized by a pronounced moisture-sensitivity due to the inherent hydrolytic instability

imposed by the presence of several Si-N bonds in the molecules.

Homogeneous catalysts for stereoregular olefin polymerization are further disclosed in U.S. Pat. No. 5,330,948. According to this patent, by using a metallocene catalyst having a chiral substituent selected from neomenthyl, 5 menthyl and phenylmenthyl with a cocatalyst, better control over the desired properties of the resulting polymer is achieved.

U.S. Pat. No. 5,594,080 describes metallocene catalysts bearing cyclopentadienyl-type ligands, which are used in the production of elastomeric polyolefins. The structure and therefore the properties of the obtained products 10 depend on several factors, inter alia the olefin monomer pressure during the polymerization and the nature of the cyclopentadienyl-based ligands.

The synthesis of stereoregular polymers has been reported (M. Bochmann, J. Chem. Soc., Dalton Trans. 225, (1996); H. H. Brintzinger, D. Fischer, R. Müllhaupt, B. Rieger and R. M. Waymouth, Angew. Chem., Int. Ed. 15 Engl. 34, 1143 (1995)) by using chiral organo-group IV (Ti, Zr, Hf) catalysts having approximate C_2 symmetry. Most of the ligands for these " C_2 " catalysts are based upon indenyl or related cyclopentadienyl components and are difficult and expensive to synthesize.

Octahedral transition-metal complexes for use in homogeneous catalyst 20 systems for the polymerization of alpha-olefins are known. EP-A-0 675138 discloses the use of a catalyst comprising the cationic form of benzamidinato octahedral transition metal complexes and an anion of a Lewis acid or Brönsted

acid for the polymerization of alpha-olefins including propylene. The polymerization reaction can be carried out at a pressure in the range from atmospheric pressure to 200 kg/cm²G. Although the polymerization catalyst disclosed is a cationic form of an octahedral transition metal complex, and the 5 homopolymerization of propylene is specifically disclosed, there is no mention of the tacticity of the polymer, and more specifically, there is no teaching of the tacticity characteristics of the polymer as a function of the olefin monomer or pressure.

EP-A-0 687693 describes the use of amidinato catalyst systems for the 10 polymerization of alpha-olefins. Among possible cocatalysts, alumoxanes and boron compounds are mentioned. The alpha-olefins to be polymerized have at least 3 carbon atoms, and the polymerization can be carried out at a pressure of from 1 to 3000 bar. As with EP-A-0 675138, there is no indication of the tacticity characteristics of the polymer, nor is it suggested how the tacticity 15 characteristics of the polymer may depend on the pressure or partial pressure of the olefin monomer. There is certainly no indication that the catalyst systems and operating conditions can be designed to produce polymers and copolymers having specific, desired tacticities. Furthermore, the formation of elastomers from homogeneous catalyst systems of this type is unknown.

20 There is thus a great need for, and it is highly desirous to have, inexpensive, moisture-insensitive catalyst systems that enable the production of stereoregular poly alpha-olefins in an efficient manner, with high conversions

and yields, and a need for efficient methods of producing these stereoregular poly alpha-olefins. There is also a great need for catalyst systems and methods for the production of elastomeric poly alpha-olefins. Moreover, it would be highly advantageous to have catalyst systems and methods for the production of 5 poly alpha-olefins in which the tacticity -- qualitative and quantitative -- of the polymers could be predicted and produced using rational design.

SUMMARY OF THE INVENTION

10 Accordingly, it is an object of the present invention to provide a method of polymerization of one or more alpha-olefins to form polymers having a preselected range of properties, ranging from isotactic to elastomeric properties.

15 It is another object of the invention to provide improved, low-cost homogeneous precatalysts for polymerization, which, when used with an appropriate cocatalyst, permit the efficient polymerization of alpha-olefins to produce highly stereoregular polymers.

20 It is another object of the invention to provide improved, low-cost homogeneous precatalysts for polymerization, which, when used with an appropriate cocatalyst, permit the efficient polymerization of alpha-olefins to produce elastomeric polymers.

It is another object of the invention to provide a new class of catalysts, which, as contrasted to the known catalysts that contain cyclopentadienyl ligands, are not decomposed when exposed to air or humidity.

Thus, according to the teachings of the present invention there is provided a process for the polymerization of one or more alpha-olefins having at least 3 carbon atoms, the process comprising the steps of (a) contacting the monomer or monomers in a solvent selected from the group consisting of polar and non-polar solvents under polymerization conditions with a homogeneous catalyst system including (i) a cationic form of a chiral or a non chiral octahedral transition metal complex, comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands and having symmetry selected from the group consisting of C_1 , C_2 , and C_3 symmetries; and (ii) an anion of an acid selected from the group consisting of a Lewis acid and a Brønsted acid; and (b) adjusting the pressure to obtain either a highly stereoregular polymer, a copolymer or an elastomer.

The homogeneous catalyst system can include a racemic or non-racemic mixture of said chiral octahedral transition metal complex.

According to the teachings of the present invention there is further provided a homogeneous catalyst system comprising (a) a cationic form of a chiral octahedral transition metal complex comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands and having symmetry selected from the group consisting of C_1 , C_2 , and C_3 symmetries; and (b) an anion of an acid selected from the group consisting of a Lewis acid and a Brønsted acid.

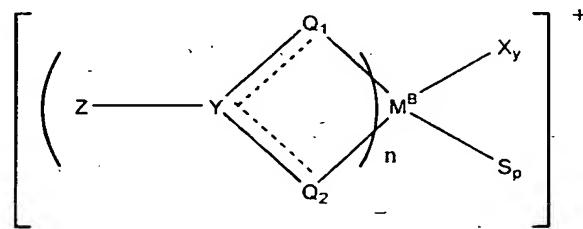
In a preferred embodiment, the symmetry of the homogeneous catalyst

system is C_1 symmetry. In another preferred embodiment, the symmetry of the homogeneous catalyst system is C_2 symmetry. In yet another preferred embodiment, the symmetry of the homogeneous catalyst system is C_3 symmetry.

5 In a preferred embodiment, the cationic form of the transition metal component of the catalyst system utilized in the above-mentioned process can be represented by formula A or formula B:

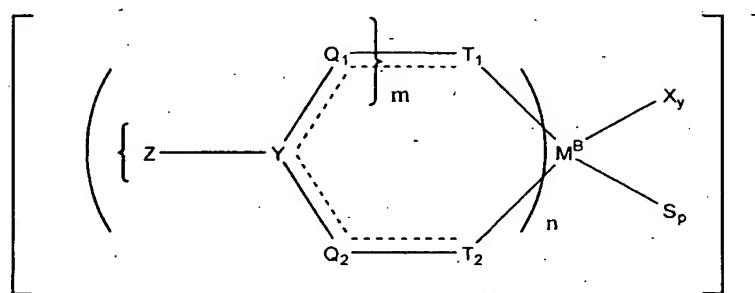
Formula A:

10



Formula B:

15



20 wherein X is an anionic ligand; M is a transition metal atom selected from groups III, IV, and V of the periodic table of elements; B, the valency of M,

10

equals 3, 4 or 5; Y is C, N, S, P, B or Si; Q₁, Q₂, T₁ and T₂ are each independently selected from the group consisting of O, OR, N, NR, NR₂, CR, CR₂, S, SR, SiR₂, B, BR, BR₂, P, PR and PR₂, where each R is independently H or a group containing C, Si, N, O, B and/or P, whereas one or more R groups 5 may be attached to M, each replacing the anionic ligand identified herein by X; Z is selected from H, OR, NR₂, CR, CR₂, CR₃, SR, SiR₃, PR₂ or BR₂; S is a solvent molecule; m is an integer selected from the group consisting of 1, 2, 3 or 4; n is an integer selected from the group consisting of 1, 2 or 3; y equals (B-n-1); and p is 0 or an integer to satisfy octahedral coordination requirements 10 of the transition metal atom M.

In a preferred embodiment, the octahedral transition metal complexes characterized by formula A and formula B are of C₁ symmetry, n equals one, and the transition metal is selected from the group consisting of zirconium and hafnium. The application of high pressure produces poly alpha-olefins that are 15 substantially elastomeric.

In another preferred embodiment, the octahedral transition metal complex has C₂ or C₃ symmetry and the transition metal is selected from the group consisting of zirconium and hafnium. At high pressure, substantially pure isotactic poly alpha-olefins are obtained. At low pressure, non-stereoregular (atactic-type) poly alpha-olefins are obtained. When the pressure 20 is alternated between high pressure and low pressure, an elastomer with atactic and isotactic segments is produced. The pressure alternation is preferably

performed at a frequency lower than or about equal to the polymerization insertion rate. In a preferred embodiment, the alternation of pressure is carried out at a frequency of about 10^{-4} to 100 Hertz.

Homogeneous catalyst systems for the production of stereoregular 5 poly alpha olefins that include a cationic form of a chiral octahedral transition metal complex or a racemic mixture of an octahedral transition metal complex were not known prior to their disclosure in Israel Patent Application Serial No. 121402 and Israel Patent Application Serial No. 122105, from which the instant application claims priority. Moreover, according to known theory, a 10 homogeneous catalyst system including a cationic form of a racemic mixture of an octahedral transition metal complex having C_1 symmetry should produce isotactic (stereoregular) alpha-olefins; a non-chiral octahedral transition metal complex having C_{2v} symmetry (or higher) should produce atactic alpha-olefins. By contrast, it has been discovered by the inventors of the instant invention 15 that, at high pressures, homogeneous catalyst systems (of the present invention) which include a cationic form of octahedral zirconium or octahedral hafnium metal complexes having C_1 symmetry and one bidentate chelating ligand, produce elastomers.

In a preferred embodiment, the transition metal of the octahedral 20 complex is selected from the group consisting of vanadium, niobium, tantalum, scandium, yttrium, lanthanum, lanthanides, and actinides.

In this respect, the behavior of titanium would be expected to be

qualitatively similar to that of zirconium and hafnium, because titanium, zirconium and hafnium belong to the same transition metal family and because they have been used in a substantially identical fashion in the polymerization of alpha-olefins with conventional Ziegler-Natta catalysts. It has been discovered, 5 however, that at high pressure, homogeneous catalyst systems that include a cationic form of (chiral and non-chiral) octahedral titanium metal complexes of the present invention produce elastomers. The formation of elastomers using said octahedral titanium metal complexes is substantially irrespective of symmetry (C₁, C₂, and C₃) and solvent. Alteration of pressure is unnecessary, 10 such that operation is greatly simplified.

Hence, further according to the teachings of the present invention there is provided a process for the polymerization of one or more alpha-olefins having at least 3 carbon atoms, comprising contacting alpha-olefin monomer or monomers in a solvent selected from the group consisting of polar solvents and 15 non-polar solvents under polymerization conditions and above atmospheric pressure with a homogeneous catalyst system, said homogeneous catalyst system including: (i) a cationic form of a chiral or a non chiral octahedral titanium complex, comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands; and (ii) an anion of an acid selected from the group 20 consisting of a Lewis acid and a Brønsted acid, to obtain an elastomer.

In a preferred embodiment, the homogeneous catalyst system includes a racemic or non-racemic mixture of said chiral octahedral titanium complex.

Further provided is a homogeneous catalyst system including: (a) a cationic form of an octahedral titanium complex having C_s symmetry, and (b) an anion of an acid selected from the group consisting of a Lewis acid and a Brönsted acid.

5 Further provided is a process for the polymerization of one or more alpha-olefins having at least 3 carbon atoms, comprising contacting alpha-olefin monomer or monomers in a solvent selected from the group consisting of a polar solvent and a non-polar solvent under polymerization conditions, at or above atmospheric pressure, with a homogeneous catalyst system, said

10 homogeneous catalyst system including: (i) a cationic form of an octahedral titanium complex having C_s symmetry; and (ii) an anion of an acid selected from the group consisting of a Lewis acid and a Brönsted acid, to obtain an elastomer.

It has been discovered by the inventors of the instant invention that a
15 chiral, octahedral transition metal complex having C_1 or C_2 symmetry is used to obtain syndiotactic polystyrene of very high stereoregularity. The activity of such complexes is over an order of magnitude higher than the activities of non-chiral octahedral complexes of the prior art (2.5×10^6 - 1×10^7 in the instant invention vs. 1.2×10^5 - 5.5×10^5). The stereoregularity of the polystyrene
20 produced in processes of the instant invention is also superior to that of prior-art processes.

Hence, further provided is a polymerization process comprising the steps

of contacting styrene monomer or monomers comprising styrene in a solvent selected from the group consisting of polar and non-polar solvents under polymerization conditions and at a pressure of about atmospheric or higher with a homogeneous catalyst system including: (i) a cationic form of a chiral 5 octahedral transition metal complex comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands and having symmetry selected from the group consisting of C_1 and C_2 symmetries, and (ii) an anion of an acid selected from the group consisting of a Lewis acid and a Brönsted acid, to obtain syndiotactic polystyrene or a copolymer comprising syndiotactic polystyrene.

10 In a preferred embodiment of the invention, an octahedral complex having C_1 or C_2 symmetry is used at low pressure to obtain an elastomeric copolymer containing sequences of syndiotactic polystyrene and atactic poly-aliphatic alpha-olefins. Propylene is a preferred aliphatic alpha-olefin.

In another preferred embodiment, an octahedral complex having C_1 or 15 C_2 symmetry is used at alternating pressure to obtain an elastomeric copolymer containing sequences of syndiotactic polystyrene and isotactic and atactic sequences of poly-aliphatic alpha-olefins. Propylene is a preferred aliphatic alpha-olefin for this embodiment.

It has been found that homogeneous catalyst systems having cationic 20 octahedral transition metal complexes (of the present invention) and possessing C_1 , C_2 or C_3 symmetry are suitable for hydrogenation reactions. Racemic mixtures of C_2 -symmetry complexes and monoheteroallylic complexes have

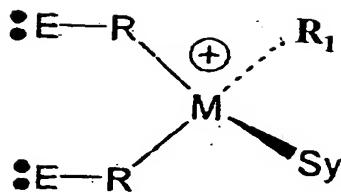
been found to be particularly suitable.

As described above, the present invention largely relates to homogeneous catalyst systems having cationic octahedral transition metal complexes and to processes utilizing such systems to produce materials of 5 desired tacticity: stereoregular polymers or elastomeric polymers. By sharp contrast, according to known theory and experimentation, tetrahedral transition metal complexes produce atactic polymers.

Surprisingly, it has been discovered that tetrahedral transition metal complexes of a particular structure can produce elastomeric polymers. 10 Moreover, the elastomeric polymers are of a novel and significant variety.

Hence, a process is provided for the polymerization of alpha-olefins having at least 3 carbon atoms is herein provided, comprising contacting the alpha-olefin monomer in a solvent selected from the group consisting of polar solvents and non-polar solvents under polymerization conditions, at or above 15 atmospheric pressure, with a homogeneous catalyst system comprising (a) a cationic form of a tetrahedral complex having (i) a transition metal center, and (ii) one or more Lewis basic pendant groups capable of donating one or more pairs of free electrons to the transition metal center; and (b) an anion of an acid selected from the group consisting of a Lewis acid and a Brönsted acid, to 20 obtain an elastomer.

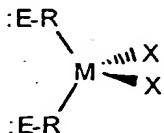
In a preferred embodiment, the cationic form of the tetrahedral complex is of the form:



wherein:

5 E is a donating group with a free pair of electrons; R₁ is selected from the group consisting of H, alkyl, aryl and silyl; S is a solvent molecule; y is 0 or 1; and R is C, B, N, P, O, S or any other anionic bridging group.

Preferably, the tetrahedral complex is of the form:



10 wherein: X is a halide; E is a donating group with a free pair of electrons; and R is C, B, N, P, O, S or any other anionic bridging group.

The process and mechanism thereof are developed further in the detailed description of the invention provided below. From the detailed description taken in conjunction with the figures and the appended claims, additional 15 objects and advantages of the invention will be apparent to those skilled in the art.

As used herein in the specification and claims section below, the phrase "stereoregular" refers to a regular spatial ordering of pendant groups from the main backbone of the polymer; "isotactic" ordering is a stereoregular 20 arrangement in which the pendant groups are arranged in space toward the

same side of the backbone; "syndiotactic" ordering is a stereoregular arrangement in which the pendant groups are arranged around the backbone in an alternating form.

As used herein in the specification and claims section below, the phrases

5 "elastomer", "elastomeric polymer" and the like refer to poly alpha-olefins having elastomeric properties, including the tendency to revert to the original shape after extension. Such elastomers are obtained in various ways, including the production of polymer chains having stereosequences alternating between crystalline stereoregular (e.g., isotactic or syndiotactic) and amorphous atactic.

10 Elastomers can also be obtained by stereoregular "mistakes" that are incorporated into sequences that are otherwise stereoregular. Such mistakes are often produced by complexes that exhibit high kinetic activities.

As used herein in the specification and claims section below, the term "symmetry" is used in accordance with the standard definition and usage: the

15 symmetry C_n of a given molecule defines the number of times the original figure is reproduced during a complete rotation. The symmetry angle is $2\pi/n$ such that for C_1 , the symmetry is 2π or 360° ; for C_2 , the symmetry is 180° ; for C_3 , the symmetry is 120° . Other, more specialized symmetries include C_{2v} , which has C_2 symmetry combined with vertical symmetry, and C_s which has

20 mirror-image symmetry.

As used herein in the specification and claims section below, the phrase "natural chiral center" refers to a carbon or to a metal in which the mirror image

with all the substituents is not superimposable. A carbon center is not superimposable when surrounded by four different substituents. For metal centers, however, superimposability depends on the particular symmetry of the complex. Chiral complexes, by definition, are not superimposable.

5 As used herein in the specification and claims section below, the phrase "low pressure" refers to pressures below about 1 atmosphere; the phrase "high pressure" refers to pressures above about 1 atmosphere and preferably, to pressures above about 2 atmospheres. "Pressure" typically refers to the partial pressure of the monomer species, which affects the concentration of monomer
10 in solution. However, the total absolute pressure also influences the equilibrium between the monomer concentration in solution to the monomer concentration gas-phase.

The phrase "alternating pressure" as used herein in the specification and claims section below, refers to a repetitive change of pressure from low to high
15 and/or vice versa.

The phrase "bidentate chelating ligands", as used herein in the specification and claims section below, and as demonstrated in the plurality of examples provided herein, refers solely to monoanionic ligands.

20 BRIEF DESCRIPTION OF THE DRAWINGS

The invention is herein described, by way of example only, with reference to the accompanying drawings. With specific reference now to the drawings in detail, it is stressed that the particulars shown are by way of

example and for purposes of illustrative discussion of the preferred embodiments of the present invention only, and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this 5 regard, no attempt is made to show structural details of the invention in more detail than is necessary for a fundamental understanding of the invention, the description taken with the drawings making apparent to those skilled in the art how the various forms of the invention may be embodied in practice.

In the drawings:

10 FIGs. 1a-c are schematic illustrations of octahedral transition metal complexes comprising bidentate chelating ligands arranged around the coordination sphere of the metal (M), wherein FIG. 1a provides a complex with one bidentate chelating ligand; FIG. 1b provides a complex with two bidentate chelating ligands; and FIG. 1c provides a complex with three bidentate 15 chelating ligands;

FIG. 2 is a schematic illustration of racemic octahedral complexes;

FIG. 3 provides a schematic representation of Ti and Zr complexes containing bulky benzamidinate ligands, according to the present invention;

20 FIG. 4 illustrates the competing reactions of intramolecular epimerization reaction of the growing polypropylene chain at the last-inserted monomer unit, vs. the stereoregular insertion of propylene;

FIG. 5 illustrates, by way of example, the dynamic equilibrium between

tetrahedral transition metal complexes having a particular structure (defined below) and octahedral transition metal complexes leading to competing mechanisms of isotactic and atactic insertions.

5 DESCRIPTION OF THE PREFERRED EMBODIMENTS

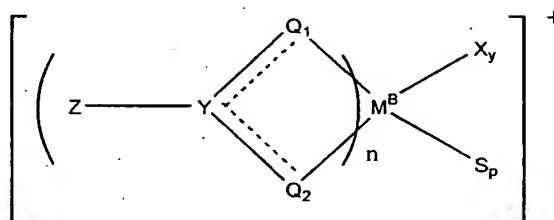
The present invention teaches (i) the use of certain octahedral transition metal complexes as precatalysts for the stereoregular and/or elastomeric polymerization of alpha-olefins; (ii) the use of homogeneous catalyst systems comprising these complexes; (iii) novel classes of such complexes; and (iv) the use of a specific class of tetrahedral transition metal complexes as precatalysts for the production of elastomeric poly alpha-olefins.

The principles of producing stereoregular and elastomeric polymers and copolymers according to the present invention may be better understood with 15 reference to the drawings and the accompanying description.

A. The cationic form of the transition metal component

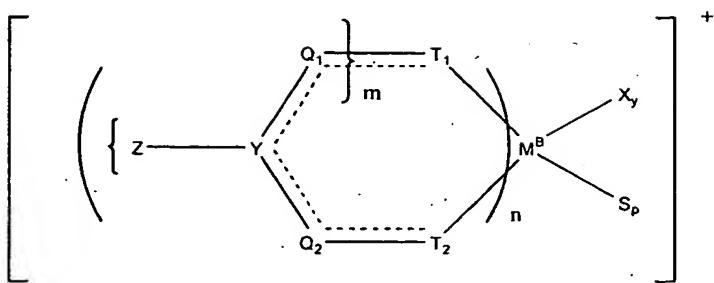
Preferred embodiments of the cationic form of the transition metal component of the homogeneous catalyst system of the present invention can be represented by formula A or formula B:

Formula A:



Formula B:

5



wherein X is an anionic ligand; M is a transition metal atom selected from groups III, IV, and V of the periodic table of elements; B, the valency of M, equals 3, 4 or 5; Y is C, N, S, P, B or Si; Q₁, Q₂, T₁ and T₂ are each independently selected from the group consisting of O, OR, N, NR, NR₂, CR,

10 CR₂, S, SR, SiR₂, B, BR, BR₂, P, PR and PR₂, where each R is independently H or a group containing C, Si, N, O, B and/or P, whereas one or more R groups may be attached to M, each replacing the anionic ligand identified herein by X; Z is selected from H, OR, NR₂, CR, CR₂, CR₃, SR, SiR₃, PR₂ or BR₂; S is a solvent molecule; m is an integer selected from the group consisting of 1, 2, 3 or 4; n is an integer selected from the group consisting of 1, 2 or 3; y equals (B-n-1); and p is 0 or an integer to satisfy octahedral coordination requirements of the transition metal atom M.

20 A particularly interesting class of complexes are those wherein Z and/or Q have natural chirality center(s), for example, menthyl, neomenthyl, myrtanyl and/or alpha-phenethyl groups. These chiral substances are found in nature, they are inexpensive, yet more importantly they were both unexpectedly found to be highly effective while implementing the process of the present invention.

As can be seen in Figure 1a, for n=1, when R* is a chiral group, the octahedral complexes that are obtained are chiral with a C₁ symmetry in all cases. When R* is non chiral, the complex provided in FIG. 1 (a) has a symmetry of C_s or higher (depending on the rest of the ligands). As can be seen in Figure 1b and 1c, for n=2 and n=3, respectively, when R* is a chiral group, a mixture of diastereomeric complexes having C₂ and C₃ symmetries, respectively, can be expected. When R* is a non-chiral group, the complexes are racemic mixtures of complexes with C₂ and C₃ symmetry, respectively, as illustrated in Figures 1b and 1c. As an additional example, a racemic mixture 10 of octahedral complexes having C₂ symmetry is provided in Figure 2.

B. Preparation of the complex:

The complexes according to the present invention can be prepared by known methods, e.g., those described in J. Organometallic Chem. 503, 307 (1995) and in the references mentioned therein, all of which are incorporated by 15 reference as if fully set forth herein.

By way of example, the complex wherein the ligand comprises a chiral substituent R* such as menthyl, myrtanyl or phenethyl, is obtained by reacting a chiral amine with a compound containing a group such as alkyl, aryl or trimethylsilyl halide, in a high-boiling polar solvent such as tetrahydrofuran 20 (THF). The resulting chiral amine compound, combined with an alkyl lithium complex and further with a nitrile group in a polar solvent such as dimethoxyethane (DME), dimethyl ether, or tetrahydrofuran, will produce a

lithium salt. This salt may be either reacted with an equimolar amount of water to obtain the free ligand or with a compound of the general formula MX'_4 , wherein M is a cation derived from a transition metal, for example Ti, Zr or Hf, and X' is a halogen, e.g., Cl, Br or I (MX'_4 preferably being $ZrCl_4$) in a polar or 5 non polar solvent. Examples of such solvents are diethyl ether, pentane, toluene, THF, DME, etc. The free ligand may be reacted with a compound of the general formula MX''_4 , wherein M is a cation derived from a transition metal, for example Ti, Zr or Hf, and X'' is an amido, phosphido, alkyl or aryl group (MX''_4 preferably being $Zr(N(CH_3)_2)_4$) in a polar or non-polar solvent. 10 Examples of such solvents include diethyl ether, pentane, toluene, THF and DME.

According to one embodiment of the present invention, the halogen may be replaced by various alkyl, aryl, amine or phosphine groups.

A series of Ti and Zr complexes containing bulky benzamidinate ligands 15 has been prepared while reducing the present invention to practice. To this end, $TiCl_4(THF)_2$ or $ZrCl_4(THF)_2$ were reacted with two equivalents of $Li[C_6H_5C(NC_3H_7)_2]$ or $Li[C_6H_5C(NC_6H_{11})_2]$, producing in crystalline form the four bis-ligand complexes provided in Figure 3.

By analogy, the reaction of $ZrCl_4$ with two equivalents of the substituted 20 bis(trimethylsilyl)benzamidinate lithium-TMEDA complex (TMEDA- N,N,N',N' -tetramethylethylenediamine) yielded zirconium dichloride complexes in a crystalline form.

The cationic forms of the catalysts were generated by the reaction of the corresponding complexes with the cocatalyst:

C. The Cocatalyst:

The catalyst system employed in the present invention comprises a complex of the transition metal component and a cocatalyst in an excess ratio for alumoxane cocatalysts and equimolar ratios for other Lewis acids or Brønsted acids cocatalysts. In a preferred embodiment, the co-catalyst includes oligomeric alumoxanes and alkylalumoxanes such as methyl alumoxane (MAO), or perfluoroaromatic boron compounds such as $B(C_6F_5)_3$, tris(perfluoro)naphtylborane, and tris(perfluoro)dibenzylborane. The methyl alumoxane should preferably have an average degree of oligomerization of from about 13 to about 25.

Brønsted acids that are particularly suitable as cocatalysts include those belonging to the families of trialkylammonium tetra(perfluoro)naphtylborates and trialkylammonium tetra(perfluoro)dibenzylborates, $(Et_3N)HB(C_6F_5)_4$, as well as, for example, $HN(CH_3)_3^+B(C_6F_5)_4^-$, $HN(CH_3)_3^+Al(C_6F_5)_4^-$, and $HP(CH_3)_3^+Al(C_6F_5)_4^-$.

D. The polymerization process:

The polymerization process of the present invention is effected by contacting an olefin monomer or mixture of monomers with the catalyst system in a suitable organic solvent; and thereafter reacting the monomer(s) in the

presence of the catalyst system under atmospheric pressure and/or elevated pressures, for a period and at a temperature sufficient to produce a polymer.

While reducing the present invention to practice, polymerizations were carried out under rigorously anaerobic/anhydrous vacuum line conditions, and 5 reactions were quenched after appropriate times with methanol-HCl solutions prior to collection of the polymer, followed by washing with pentane and acetone and drying.

The monomer for the polymerization process is an alpha-olefin having at least three carbon atoms, such as propylene, 1-butene, 1-isobutylene, 1-pentene, 10 4-methyl-1-pentene, 1-hexene, 1,5-hexadiene, styrene or mixtures thereof.

In metallocene catalysts of the prior art, polymer tacticity has been found to vary predictably with the structure of the metallocene catalysts. Complexes with C_2 or C_1 symmetry are expected to produce isotactic polyolefins, complexes with C_s symmetry are expected to produce syndiotactic polyolefins, 15 whereas those with C_{2v} symmetry and higher generate atactic polymers (M. Bochmann, J. Chem. Soc., Dalton Trans. 225, (1996); H. H. Brintzinger, D. Fischer, R. M?llhaupt, B. Rieger and R. M. Waymouth, Angew. Chem., Int. Ed. Engl. 34, 1143 (1995)); M?hring, P. C.; Coville, N. J., J. Organomet. Chem. (1994), 479, 1). Surprisingly, however, when the polymerization of propylene 20 is carried out at atmospheric pressure with an octahedral complex having C_2 symmetry, atactic polypropylene is formed as an oil, instead of the expected isotactic polymer. Without wishing to be limited by the theoretical explanation,

it is believed that the formation of atactic polypropylene results from an intramolecular epimerization reaction of the growing polypropylene chain at the last-inserted monomer unit, the epimerization reaction being faster than the stereoregular insertion of propylene (FIG. 4).

5 While reducing the present invention to practice, it was discovered that with an octahedral complex having C_2 or C_3 symmetry, (the expected) isotactic polypropylene is formed (degree of crystallinity (mmmm) > 99.5%; mp = 161-164 °C) only when the polymerization is carried out at high concentrations of monomer (e.g., in liquid propylene). Again, without wishing to be limited by
10 the theoretical explanation, it is believed that a high propylene concentration allows faster insertion of the monomer unit, substantially suppressing the epimerization reaction.

According to the present invention, by adjusting the pressure (i.e., the partial pressure of the monomer, which effects the monomer concentration in
15 solution) of the polymerization reaction, the stereoregularity of the products may be controlled. Thus, in the polymerization of propylene and higher aliphatic olefins in the presence of a zirconium-based or hafnium-based catalyst of the present invention having C_2 or C_3 symmetry, an atactic product with an oily or amorphous appearance is produced at atmospheric pressure. On the
20 other hand, under a higher pressure of above about two atmospheres or preferably more, a highly stereoregular thermoplastic product is obtained.

When the polymerization of aliphatic olefins is carried out under a

pressure alternating between low pressure and high pressure, e.g., between a pressure below 1 atmosphere and above 2 atmospheres, an elastomeric product is obtained using zirconium-based or hafnium-based catalysts of C_2 or C_3 symmetry. Preferably, said pressure is alternated at a frequency about equal to 5 or lower than the polymerization insertion rate, e.g., between 1×10^{-4} and 100 Hertz.

Some of the examples of the production of elastomers by adjusting pressure in the presence of octahedral transition metal complexes of C_2 symmetry according to the present invention pertain to the block polymerization 10 of aliphatic alpha-olefins, wherein one or more monomers is polymerized at high pressure to produce stereoregular (isotactic) poly alpha-olefins, and the resultant product material is subjected to low-pressure polymerization conditions in the presence of one or more monomers, to produce atactic poly 15 alpha-olefins. The atactic poly alpha-olefins are incorporated in the isotactic material formed at high pressure, thereby producing an elastomeric polymer or copolymer.

According to known theory, a homogeneous catalyst system including a cationic form of a chiral octahedral transition metal complex (e.g., having C_1 or 20 C_2 symmetry) should produce stereoregular (isotactic) alpha-olefins; whereas an octahedral transition metal complex of C_{2v} symmetry and higher should produce atactic alpha-olefins. By contrast, it has been discovered while reducing the present invention to practice that homogeneous catalyst systems

which include a cationic form of chiral octahedral zirconium metal complexes of the present invention having one bidentate chelating ligand (or racemic or non-racemic mixtures thereof) and having C_1 symmetry produce elastomers. Similarly, hafnium-based complexes of the present invention having C_1 symmetry have also been found to produce elastomers.

It is anticipated that the behavior of titanium would be qualitatively similar, in this respect, to that of zirconium and hafnium, because titanium, zirconium and hafnium belong to the same transition metal family, and because they have been used in a substantially identical fashion in the polymerization of alpha-olefins with conventional Ziegler-Natta catalysts.

It has been discovered, however, that at high pressure, homogeneous catalyst systems that include a cationic form of (chiral and non-chiral) octahedral titanium metal complexes of the present invention produce elastomers. The formation of elastomers using said octahedral titanium metal complexes is substantially irrespective of symmetry (C_1 , C_2 , or C_3) and solvent. Alternation of pressure is unnecessary, such that operation is greatly simplified.

The production of elastomers with titanium-based complexes of the present invention is exemplified by the formation of elastomeric polypropylene using a titanium-based complex, $(4\text{-CH}_3\text{-C}_6\text{H}_4)\text{C}(\text{N}(\text{Si}(\text{CH}_3)_3)_2)\text{TiCl}_3\text{-THF}$. Although alternating the pressure will result in the formation of an elastomer, it was demonstrated that an elastomer can be obtained without alternating pressure from high pressure to low pressure.

The above-mentioned complex has C_s symmetry, according to known theory, should produce stereoregular (syndiotactic) poly alpha-olefins. Surprisingly, however, elastomeric polypropylene is produced. Other titanium-based complexes of different symmetries, e.g., octahedral titanium complexes 5 having C_1 symmetry, also have been found to produce elastomeric poly alpha-olefins. This, however, is not at all surprising, and indeed, could have been anticipated, with the knowledge that Ti-based octahedral complexes having C_s symmetry produce elastomers, because C_1 symmetry, like C_s symmetry, is expected to produce stereoregular poly alpha-olefins.

10 As described above, all prior-art processes utilize octahedral transition metal complexes that are non-chiral, perhaps because chiral octahedral transition metal complexes are expected to produce isotactic polystyrene. Surprisingly, therefore, chiral octahedral transition metal complexes utilized in processes according to the present invention have been found to produce highly 15 stereoregular, syndiotactic polystyrene. Moreover, the activity of the instant catalyst systems is 1-2 orders of magnitude higher than the activity of non-chiral systems of the prior art (Flores et al., “[N,N’-Bis(trimethylsilyl)benzamidinato]titanium and -zirconium Compounds. Synthesis and Application as Precursors for the Syndiospecific Polymerization 20 of Styrene”, Organometallics, 14, pp.1827-1833, 1995).

It is shown above that the expected isotactic polypropylene (mmmm > 99.5%; mp = 161. °C) can be formed when the polymerization is carried out at

high concentrations of monomer (e.g., in liquid propylene) using octahedral complexes based on zirconium or hafnium and having C₂ or C₃ symmetry. This process is attributed to the resulting high propylene concentration in solution, which speeds up the insertion of the monomeric unit, such that the competing 5 epimerization mechanism (leading to atactic polymerization) is suppressed almost completely.

It is shown herein for the first time that simple octahedral or even tetrahedral complexes which have a Lewis basic pendant group which can donate an electron lone pair to the highly electrophilic metal center can be 10 applied in the preparation of a unique type of elastomeric polymers.

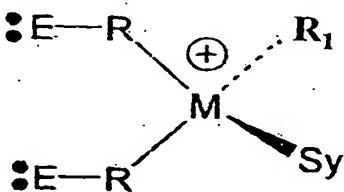
As shown in Figure 5, this is attributed to the dynamic equilibrium between the tetrahedral and octahedral configuration: when the complex is in a tetrahedral form, an atactic polymer is obtained as anticipated by known theory; when the complex is in an octahedral form, after the donating groups attach to 15 the metal center, an isotactic polymer is obtained. Without being limited by the postulated mechanism, it is believed that the dynamic equilibrium between the tetrahedral and octahedral forms induces the polymerization of an elastomeric α -olefin. This consecutive, dynamic process allows for the utilization of tetrahedral transition metal complexes for the production of a novel type of 20 elastomeric polymer. Moreover, this consecutive, dynamic process allows for the rational design of this new type of elastomeric polymers in which the degree of stereoregularity -- and hence, the elastomeric properties -- can be predicted

and tailored. For example, a tetrahedral complex can be designed such that the path via the octahedral complex is favored over the epimerization route (in terms of stability, kinetics, etc.), such that an elastomer of relatively high stereoregularity is obtained. It is also possible to design the polymerization conditions, choice of solvent (e.g., polarity) to this end. The choice of monomer or monomers should also affect the competition between the two routes and consequently, the elastomeric properties of the polymer product.

Thus, a process is provided herein for the polymerization of one or more alpha-olefins having at least 3 carbon atoms, comprising contacting alpha-olefin monomer or monomers in a solvent selected from the group consisting of polar solvents and non-polar solvents under polymerization conditions, at or above atmospheric pressure, with a homogeneous catalyst system, said homogeneous catalyst system comprising: (a) a cationic form of a tetrahedral complex having: (i) a transition metal center, and (ii) one or more Lewis basic pendant groups capable of donating one or more pairs of free electrons to the transition metal center; and (b) an anion of an acid selected from the group consisting of a Lewis acid and a Brønsted acid, to obtain an elastomer.

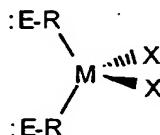
In a preferred embodiment, the cationic form of the tetrahedral complex is of the form:

20



wherein: E is a donating group with a free pair of electrons; R₁ is selected from the group consisting of H, alkyl, aryl and silyl; S is a solvent molecule; y is 0 or 1; and R is C, B, N, P, O, S or any other anionic bridging group.

Preferably, the tetrahedral complex is of the form:



5

wherein: X is a halide; E is a donating group with a free pair of electrons; and R is C, B, N, P, O, S or any other anionic bridging group.

E. Hydrogenation

10 The racemic mixture of C₂-symmetry and C₃-symmetry complexes and monoheteroallylic complexes have been found to be also useful as catalysts for the hydrogenation of olefins. Thus, in the presence of such catalysts of the present invention, ethane is formed from a mixture of ethylene and hydrogen. Since there is a competition between the insertion (polymerization) and the 15 hydrogenation processes, the reaction can be driven towards the required product by controlling the partial pressure of the gases.

The present invention will be described in more detail with the aid of the following non-limiting examples.

Thus, additional objects, advantages, and novel features of the present 20 invention will become apparent to one ordinarily skilled in the art upon

examination of the following examples, which are not intended to be limiting. Additionally, each of the various embodiments and aspects of the present invention as delineated herein above and as claimed in the claims section below finds experimental support in the following examples.

5 All manipulation of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high-vacuum (10^{-5} torr) line, or in a nitrogen-filled Vacuum Atmosphere glove box with a medium capacity recirculator (1-2 ppm O₂). Argon and nitrogen were purified by passage through

10 a MnO oxygen-removal column. Ether solvents were distilled under argon from benzophenone ketyl. Hydrocarbon solvents (toluene-d₈, C₆D₆, hexane) and TMEDA were distilled under nitrogen from Na/K alloy. All solvents for vacuum line manipulations were stored under vacuum over Na/K alloy in resealable bulbs. Nitrile compounds (Aldrich) were degassed and freshly

15 distilled under argon.

Precursors such as LiN(TMS)₂, 4-CH₃-C₆H₄-(NSiMe₃)₂Li-TMEDA, C₆H₅C[NC(i-Pr)₂]Li and C₆H₅C[NC(C₆H₁₁)₂]Li-TMEDA were prepared according to methods known in the art.

Example 1

20 *Synthesis of 4-CH₃C₆H₄C(NSiMe₃)₂Li-TMEDA*

15.86g (0.095 mol) of LiN(trimethylsilyl)₂ were stirred in a hexane suspension (180 ml) at 0 °C and then 11.1 g (0.095 mol) of 4-

methylbenzonitrile were slowly added. The temperature of the mixture was slowly raised to about 50 °C and stirred for three additional hours.

After cooling to room temperature, 14.48 g (0.123 mol) of TMEDA were added and the solution was stirred for about one hour. During the 5 addition of the TMEDA, the color of the solution turned brown-red and after several minutes, a large amount of the above product precipitated. The solution stood overnight at about 50 °C and was filtered while cold. The precipitate was dried under a high vacuum, and 31.6 g of a white crystalline product (corresponding to a yield of 83 %) was obtained.

10

Example 2

Synthesis of dichloro-bis(N,N'-trimethylsilyl-4-methyl-benzamidinato)-Zr(IV)

To a solution of 5.96 g (15.8 mmol) of $ZrCl_4(THF)_2$ in 130 ml of THF, a solution of 12.66 g (31.6 mmol) of $Li[4-CH_3C_6H_5C(NSi((CH_3)_3)_2] \cdot TMEDA$ in 100 ml of THF was added while stirring. The reaction mixture was stirred 15 overnight at room temperature and the solvent was removed under vacuum. The residue obtained was extracted with 80 ml of toluene and the precipitated LiCl was removed by filtration through a thin layer of Celite filter-aid. The clear filtrate was evaporated to dryness, washed with 20 - 30 ml of hexane and dried under vacuum for about 12 hours, obtaining 9.7 g of a yellow product 20 (corresponding to a yield of 86 %).

*Example 3**Synthesis of dichloro-bis(N,N'-dicyclohexylbenzamidinato)-titanium(IV)*

To a solution of 5.27 g (15.8 mmol) of $\text{TiCl}_4(\text{THF})_2$ in 130 ml of THF, a solution of 9.97 g (34.3 mmol) of $\text{Li}[\text{C}_6\text{H}_5\text{C}(\text{NC}_6\text{H}_{11})_2]$ in 100 ml of THF was 5 added while stirring. The reaction mixture was stirred overnight at room temperature and the solvent was removed under vacuum. The residue obtained was extracted with 80 ml of toluene and the precipitated LiCl was removed by filtration through a thin layer of Celite filter-aid. The clear filtrate was evaporated to dryness, washed with 20 - 30 ml of hexane and dried under 10 vacuum for about 12 hours, obtaining 9.2 g of a red product (corresponding to a yield of 84.5 %).

*Example 4**Synthesis of dichloro-bis(N,N'-diisopropylbenzamidinato)-zirconium(IV)*

To a solution of 7.54 g (20.0 mmol) $\text{ZrCl}_4(\text{THF})_2$ in 130 ml THF, a 15 solution of 8.41 g (40.0 mmol) of $\text{Li}[\text{C}_6\text{H}_5\text{C}(\text{NC}_3\text{H}_7)_2]$ in 100 ml of THF was added dropwise at room temperature over a period of 15 minutes. The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum, and the residue extracted with 80 ml of toluene. The precipitated LiCl was removed by filtration through a thin layer of Celite filter-aid. The clear filtrate was evaporated to dryness, washed with hexane (20-30 20 ml) and dried under vacuum for about 12 hours, thus obtaining 6.78g (corresponding to a yield of 60%) of a pale yellow, crystalline powder.

*Example 5**Synthesis of dichloro-bis(N,N'-dicyclohexyl-benzamidinato) zirconium(IV)*

To a solution of 5.96 g (15.8 mmol) $\text{ZrCl}_4(\text{THF})_2$ in 130 ml THF, a solution of 9.97 g (34.3 mmol) $\text{Li}[\text{C}_6\text{H}_5\text{C}(\text{NC}_6\text{H}_{11})_2]$ in 100 ml THF was added 5 dropwise. The reaction mixture was stirred overnight at room temperature. The solvent was removed by vacuum, and the residue was extracted with 80 ml of toluene. The precipitated LiCl was filtered through a thin layer of Celite filter-aid. The clear filtrate was evaporated to dryness, washed with hexane (20-30 ml) and dried under vacuum for about 12 hours, thus obtaining 9.02 g 10 (corresponding to a yield of 78%) of a red product.

*Example 6**Synthesis of dichloro-bis(N,N'-diphenylbenzamidinato)-zirconium (IV)*

To a solution of 6.49 g (17.2 mmol) $\text{ZrCl}_4(\text{THF})_2$ in 130 ml THF, a solution of 9.53 g (34.3 mmol) $\text{Li}[\text{C}_6\text{H}_5\text{C}(\text{NC}_6\text{H}_5)_2]$ in 100 ml THF was added 15 dropwise. The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum and the residue extracted with 80 ml of toluene. The precipitated LiCl was filtered through a thin layer of Celite filter-aid. The clear filtrate was evaporated to dryness, washed with hexane (20-30 ml) and dried under vacuum for about 12 hours, thus obtaining 9.62 g 20 (corresponding to a yield of 80%) of a pale-yellow product.

*Example 7**Polymerization of an olefin*

Six mg ($8.23 \cdot 10^{-3}$ mmol) of the catalyst described in Example 5 and 200 mg of MAO were introduced into the reactor, pumped-down and back-filled 5 three times. The flask was reevacuated and 30 ml of toluene (dried over Na/K), or CH_2Cl_2 (dried over CaH_2), were transferred by vacuum into the reactor. A large excess of gaseous propylene was introduced to the reactor at -78°C through a gas purification column. The reactor was heated to the required 10 temperature and the gas pressure was obtained from the well-known pressure-temperature relationships. Upon reaching temperature equilibration, the solution was stirred rapidly, and after a period of about two hours, the polymerization was quenched by injecting a mixture of methanol/HCl.

The polymeric product was filtered, washed with acetone and pentane and dried under vacuum. The methanol-insoluble fraction (more than 98% of 15 the product) was extremely crystalline; as measured by ^{13}C NMR spectroscopy, the product material was 98.5% isotactic. The DSC melting point was between 161°C and 165°C.

*Example 8**Olefin copolymerization*

20 Six mg ($8.23 \cdot 10^{-3}$ mmol) of the catalyst described in Example 5 and 200 mg of methylalumoxane (MAO) were introduced into the reactor and connected to a high vacuum line. The reactor vessel was pumped-down and back filled

three times, the flask was evacuated, and 30 ml of toluene (dried over Na/K) were transferred by vacuum into the reactor.

A mixture of gaseous propylene and butene (50%/50%), with a large excess with respect to both components, was introduced into the reactor 5 through the gas purification column. The reactor was heated to room temperature, resulting in a pressure of about 12 atm. After temperature equilibration, the solution was stirred rapidly for about 2 hours, and the polymer obtained was quenched by injecting a mixture of methanol/HCl. A copolymer of isotactic polypropylene-butylene was produced.

10 The co-polymer was filtered, washed with acetone and pentane, and dried under vacuum. The methane-insoluble fraction (amounting to more than 90% of the product) was of extremely high crystallinity, with an isotacticity of between 98% - 99% as determined by ^{13}C NMR spectroscopy.

In a similar manner, a block copolymerization is obtained by first 15 reacting 100% of the propylene at high pressure and then carrying out the reaction under an atmosphere of 100% butene, followed by quenching of the obtained product material.

Example 9

Olefin hydrogenation

20 Six mg ($10.5 \cdot 10^{-3}$ mmol) of the catalyst described in Example 4 and 200 mg of MAO were introduced into a reactor containing a magnetic stirring bar. The reactor was connected to a high vacuum line, pumped-down and back-

filled three times. The vessel was evacuated and 30 ml of toluene (dried over Na/K) or pentane were added by vacuum therein. A mixture of gaseous propylene and hydrogen gas (50%/50%) was introduced into the reactor through a gas purification column. The hydrogenation started almost 5 immediately and could be monitored manometrically to completion.

Example 10

Preparation of a rubbery polymer

Six mg ($8.36 \cdot 10^{-3}$ mmol) of the catalyst described in Example 2 and 200 mg of MAO were charged in the reactor connected to a high vacuum line, 10 pumped down and back-filled three times. The flask was evacuated and 30 ml of toluene (dried over Na/K) or CH_2Cl_2 (dried over CaH_2) were vacuum transferred into the reactor. Propylene was introduced into the reactor, and the temperature equilibrated to about 50 °C. (For higher-order alpha-olefins, the reaction was performed at higher temperatures such that the monomer 15 concentration in solution could be strongly influenced by pressure.) Upon adjusting the vessel pressure to 10 atmospheres, the polymerization started immediately. Afterwards, the pressure was reduced by means of a piston to atmospheric pressure and back to high pressure at a frequency of 5 fluctuations per minute.

20 An atactic polymer was obtained at atmospheric pressure, while a stereoregular polymer was obtained at high pressure, such that by varying the pressure at the proper frequency, a rubbery polymer is produced, containing in

each individual chain, both isotactic and atactic segments. The modulus of elasticity of the propylene elastomer obtained was 2500 psi, which is substantially identical to the modulus of natural rubber and SBR polymers.

Using this method were prepared elastomeric polypropylene, polybutene, 5 polyhexene, polybutadiene, and others.

Example 11

Preparation of rubbery co-homopolymer

In a similar manner, block copolymerization is obtained by first reacting 100% propylene at high pressure and then reacting the same propylene at 10 atmospheric pressure.

Example 12

Preparation of a rubbery co-heteropolymer

The process of Example 11 was repeated, wherein first the propylene was polymerized at high pressure and then butylene was reacted at atmospheric 15 pressure, thus producing a rubbery heteropolymer.

Example 13

Preparation of a rubbery co-heteropolymer

The procedure of Example 10 was repeated using a mixture of propylene and styrene as monomers, with the polymerization being carried out in a reactor 20 at normal (atmospheric) pressure at all times. A rubbery co-heteropolymer having sequences of atactic polypropylene and syndiotactic polystyrene was obtained.

Example 14

Preparation of a rubbery homopolymer with a Ti-based complex at high pressure

Instead of using a zirconium-based catalyst under alternating pressure as
5 in Example 10, a titanium-based catalyst at high pressure was tested following
the same basic procedure. Ten mg (0.0198 mmol) of the catalyst (4-CH₃-
C₆H₄)-C(N(CH₃)₃)₂TiCl₃-THF and 300 mg of MAO were charged in the
reactor connected to a high vacuum line, pumped down and back-filled three
times, the flask was evacuated and 5 ml of toluene (dried over Na/K) or CH₂Cl₂
10 (dried over CaH₂) were vacuum transferred into the reactor. Propylene was
introduced into the reactor, and the temperature was allowed to equilibrate to
about 50°C. Upon adjusting the vessel pressure to 10.2 atmospheres, the
polymerization started immediately.

About 0.9 g of an elastomeric polypropylene was obtained and
15 characterized by ¹³C NMR spectroscopy.

Example 15

Synthesis of [CH₃C(NSiMe₃)₂]₂Zr(NMe₂)₂

To a solution of 4.27 g (16 mmol) of Zr(NMe₂)₄ in 130 ml of THF, a
solution of 6.46g (32.0 mmol) of (Me₃SiN)(Me₃SiNH)CCH₃ in 150 ml of THF
20 was added while stirring at -78°C. The reaction mixture was allowed to warm
to room temperature, and was then heated under reflux for 16 hours. The
solvent was removed under vacuum. The residue was recrystallized in a

solvent mixture of toluene:hexane (20:80%), and 6.19 g (corresponding to a yield of 64%) of a yellow-colored product was obtained.

Example 16

Polymerization of propylene using $[CH_3C(NSiMe_3)_2]_2Zr(NMe_2)_2$

5 A thick-walled glass reactor was charged in a glovebox with 10 mg of $[(Me_3SiNCH)_2CH]Zr(NMe_2)_2$ and 800 mg of MAO, removed from the glovebox and connected to a high vacuum line. To the reactor were transferred, by vacuum, 20 ml of toluene. Subsequently, 25 ml of liquid propylene were transferred to the reactor. After temperature equilibration to room temperature, 10 the solution was stirred rapidly for two hours, and the polymerization was quenched. The polymeric product was filtered and washed to obtain a highly crystalline polypropylene (mmmm 98.5%) with a melting point of 152°C.

Example 17

Preparation of $[TiCl_2\{N(PPh_2)_2\}]$

15 To a stirred solution of $[Li(THF)N(PPh_2)_2]_2$ (2.0 g, 2.16 mmol) in 50 ml THF, was added $TiCl_4$ (0.24 ml, 2.16 mmol) dropwise at room temperature. The reaction mixture was stirred overnight, the solvent removed in vacuum and the residue extracted with 30 ml of toluene. Hexane was added to the filtrate to precipitate a brown solid, which was recrystallized from dichloromethane at - 20 78°C. Yield 35%. Mp 120°C (dec.). $C_{48}H_{40}Cl_2N_2P_4Ti$ (887.5), calc. C: 64.96, H: 4.54, N: 3.16; Found, C: 64.03, H: 4.86, N: 3.01.

*Example 18**Synthesis of $[C_6H_5(N\text{-TMS})(N\text{-myrtanyl})]TiCl_3$*

To a stirred solution of 0.692 g (3.7 mmol) of $TiCl_4$ in 20 ml of tetrahydrofuran was added dropwise at room temperature, a solution of 1.7 g (3.7 mmol) of $C_6H_5C(N\text{-TMS})(N\text{-myrtanyl})Li\cdot TMEDA$ in 10 ml of tetrahydrofuran. The reaction mixture was stirred overnight, the solvent was removed by vacuum, and the residue was extracted four times with 80 ml of toluene. $LiCl$ was removed by filtration through a thin layer of dried Celite filter-aid. The clear filtrate was evaporated to dryness, washed with 30 ml of hexane, and dried under vacuum to obtain 1.83 g (corresponding to a yield of 89.2%) of a red microcrystalline complex. Found: C 51.47, H 7.03, N 4.74. Calcd. for C 52.04, H 7.09, N 5.06.

*Example 19**Polymerization of propylene using $[C_6H_5(N\text{-TMS})(N\text{-myrtanyl})]TiCl_3$*

A 100-ml heavy-wall glass reactor, equipped with a strong magnetic stirrer and flame-dried under vacuum for a few hours, was charged with 5 mg of the catalyst of Example 18 and a measured amount of MAO (ratio Ti:Al=1:400) into the glovebox. The reactor was connected to a high-vacuum line, and 20 ml of CH_2Cl_2 (dried over P_2O_5) or toluene (dried over Na/K) were condensed by vacuum transfer. After equilibration of the temperature, the reactor was cooled to 150 C, and an excess of propylene (purified by passage through a MnO oxygen-removal column and a Davison 4 molecular sieve

column) was introduced into the reactor. The temperature was raised and equilibrated using a bath equipped with a thermostat, and the pressure was controlled by means of a manometer to 10 atm. The reactor was stirred strongly for a period of few hours. The polymerization was quenched by exhausting the 5 excess propylene into a well-ventilated hood, followed by the fast introduction of 30 ml of methanol/HCl. The elastomeric polypropylene was filtered, washed several times with hexane and acetone, and dried under vacuum at 0.001 mm Hg at 60°C for several hours. The filtrate solution obtained contained no atactic or low molecular weight polymer.

10

Example 20

Polymerization of Elastomeric Polypropylene promoted by a racemic bis(benzamidinate)Ti complex (cis-[p-CH₃C₆H₄C(NSiMe₃)₂]₂TiCl₂)

The experiments were conducted in a 100 ml flamed round-bottom reaction flask attached to a high-vacuum line. In a typical experiment, 4.0 mg 15 of the catalyst and 205 mg of MAO (Zr:Al = 1:400) were charged in the flask containing a magnetic stir bar. The reaction vessel was pumped down and back filled three times with argon. The flask was re-evacuated, and a measured quantity of toluene (40 ml), dried over Na/K, was vacuum transferred into the reaction flask. Subsequently, gaseous propylene was condensed into the vessel 20 through a gas purification column. The flask was warmed to room temperature and the pressure was continuously measured by means of a manometer and maintained at 10 atm. Rapid stirring of the solution was initiated, and after a

measured time interval (2 h), the polymerization was quenched by ejecting the excess pressure of propylene and immediately injecting a mixture of methanol/HCl. The elastomeric polymeric product was collected by filtration, washed with hexane and acetone and dried under vacuum for several hours, 5 producing an elastomer with a degree of crystallinity (mmmm) of 57%. The modulus of elasticity of the elastomer was 2300 psi, which is similar to the modulus of natural rubber and SBR polymers.

Example 21

Synthesis of [C₆H₅C(N-TMS)(N-myrtanyl)ZrCl₃•THF

10 *(a chiral Zr complex having C₁ symmetry)*

To a stirred solution of 5.2 g (22.2 mmol) of ZrCl₄ in 130 ml of tetrahydrofuran was added dropwise at room temperature, a solution of 10 g (22.2 mmol) of C₆H₅C(N-TMS)(N-myrtanyl)Li TMEDA in 100 ml of tetrahydrofuran. The reaction mixture was stirred overnight, the solvent was 15 removed by vacuum, and the residue was extracted with 80 ml of toluene. LiCl was removed by filtration through a thin layer of dried Celite filter-aid. The clear filtrate was evaporated to dryness, washed with 30 ml of hexane, and dried under vacuum to obtain 9.94 g (corresponding to a yield of 75%) of a yellow microcrystalline complex. Found: C 48.12, H 6.67, N 4.54, Cl 18.00. 20 Calcd. for C 48.26, H 6.58, N 4.69, Cl 17.81.

Example 22

Polymerization of Elastomeric Polypropylene using [C₆H₅C(N-TMS)(N-myrtanyl)JZrCl₃ • THF

The experiments were conducted in a 100 ml flamed round-bottom

5 reaction flask containing a magnetic stir bar. In a typical experiment, 6.0 mg of the catalyst described in Example 21 and 240 mg of MAO (Zr:Al = 1:400) were charged in the flask. The reaction vessel was connected to a high vacuum line, pumped down and back filled three times with argon. The flask was re-evacuated and 40 ml of toluene, dried over Na/K, was vacuum transferred into

10 the reaction flask. Subsequently, gaseous propylene was condensed into the vessel through a gas purification column. The flask was warmed to room temperature and the pressure (10 atm) was continuously measured by means of a manometer. Rapid stirring of the solution was initiated and after two hours, the polymerization was quenched by ejecting the excess pressure of propylene

15 and immediately injecting a mixture of methanol/HCl. The elastomeric polymeric product was collected by filtration, washed with hexane and acetone and dried under vacuum for several hours. The degree of crystallinity of the elastomeric product was mmmm = 38%.

Example 23

20 *Synthesis of [C₆H₅C(N-TMS)(N-phenethyl)JZrCl₃ • THF*

To a stirred solution of 5.2 g (22.2 mmol) of ZrCl₄ in 130 ml of tetrahydrofuran was added dropwise at room temperature, a solution of 9.30 g

(22.2 mmol) of $C_6H_5C(N\text{-TMS})(N\text{-phenethyl})Li$ TMEDA in 120 ml of tetrahydrofuran. The reaction mixture was stirred overnight, the solvent was removed by vacuum, and the residue was extracted with 80 ml of toluene. LiCl was removed by filtration through a thin layer of dried Celite filter-aid. The 5 clear filtrate was evaporated to dryness, washed with 30 ml of hexane, and dried under vacuum to obtain 6.27 g (corresponding to a yield of 50%) of a yellow microcrystalline complex. Found: C 46.53, H 5.32, N 4.87, Cl 18.78. Calcd. for C 46.75, H 5.53, N 4.96, Cl 18.82.

Example 24

10

Polymerization of Elastomeric Polypropylene using

$[C_6H_5C(N\text{-TMS})(N\text{-phenethyl})]ZrCl_3\bullet THF$

The experimental polymerization procedure of Example 22 was duplicated using the catalyst material of Example 23. The degree of crystallinity of the elastomeric product obtained was mmmin = 42%.

15

Example 25

Styrene Polymerization

The polymerization was carried out in a 100 ml glass reactor (fully covered against light) equipped with a magnetic stirring bars. The temperature was maintained at the desired temperature (25°C) using a bath equipped with a 20 thermostat. The reactor was charged with 5 mg of the catalyst as described in Example 19 and a measured amount of MAO (ratio Ti:Al = 1: 400). The reactor was connected to a high vacuum line, and 20 ml of toluene (dried over

Na/K alloy) were condensed by vacuum transfer. After equilibration of the temperature, a measured amount of freshly distilled styrene (kept at -20°C and covered against light) was introduced into the reactor by mean of a gas-tight syringe. The temperature was raised and equilibrated by means of the 5 thermostated bath. The reactor was stirred vigorously for a period of 2 hours. The polymerization was quenched by the fast introduction of 30 ml of methanol/HCl. The polymer was filtered, washed several times with hexane and acetone, and dried under vacuum at 0.001 mm Hg at 60°C for several hours to obtain 100 % conversion of 99.9% syndiotactic polystyrene.

10

*Example 26**Preparation of polymer from $[TiCl_2\{N(PPh_3)_2\}]$*

These experiments were conducted in a 100 ml flamed round-bottom reaction flask attached to a high-vacuum line. In a typical experiment 4.0 mg of the catalyst described in Example 17 and 205 mg of MAO (Zr:Al = 1:400) were 15 charged in the flask containing a magnetic stir bar. The reaction vessel was connected to a high vacuum line, pumped down and back filled for three times with argon. The flask was re-evacuated and 40 ml of toluene (dried over Na/K alloy) was vacuum transferred into the reaction flask. Gaseous propylene was then condensed into the vessel through a gas purification column. The flask was 20 warmed to room temperature and the pressure was continuously measured by means of a manometer. After rapidly stirring the solution for 2 hours, the polymerization reaction was quenched by ejecting the excess pressure of

propylene and immediately injecting a mixture of methanol/HCl. The elastomeric polymeric product was collected by filtration, washed with hexane and acetone and dried under vacuum for several hours producing an elastomer with a degree of crystallinity (mmmm) of 45%.

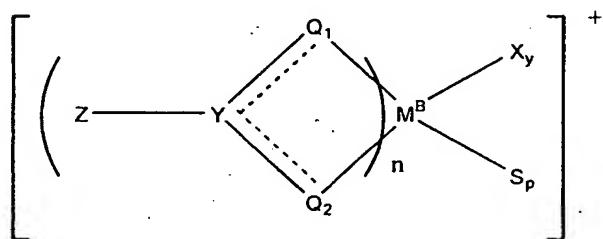
5

Although the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall 10 within the spirit and broad scope of the appended claims. All publications cited herein are incorporated by reference in their entirety. Citation or identification of any reference in this application shall not be construed as an admission that such reference is available as prior art to the present invention.

WHAT IS CLAIMED IS:

1. A process for the polymerization of one or more alpha-olefins having at least 3 carbon atoms, the process comprising the steps of:
 - (a) contacting alpha-olefin monomer or monomers in a solvent selected from the group consisting of polar solvents and non-polar solvents under polymerization conditions with a homogeneous catalyst system including:
 - (i) a cationic form of a chiral or a non chiral octahedral transition metal complex, comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands and having symmetry selected from the group consisting of C₁, C₂, and C₃ symmetries; and
 - (ii) an anion of an acid selected from the group consisting of a Lewis acid and a Brönsted acid; and
 - (b) adjusting the pressure to obtain either a highly stereoregular polymer, a copolymer or an elastomer.
2. The process according to claim 1, wherein said homogeneous catalyst system includes a racemic or non-racemic mixture of said chiral octahedral transition metal complex.

3. The process according to claim 1, wherein said cationic form of said octahedral transition metal complex has the formula:



wherein:

M is a transition metal atom selected from groups III, IV, and V of the periodic table;

B is the valency of M and equals 3, 4 or 5;

Y is selected from the group consisting of C, N, S, P, B and Si;

X is an anionic ligand;

Q₁ and Q₂ are each independently selected from the group consisting of O, OR, N, NR, NR₂, CR, CR₂, S, SR, SiR₂, B, BR, BR₂, P, PR and PR₂, where each R is independently H or a group containing C, Si, N, O, B and/or P, whereas one or more R groups may be attached to said transition metal atom M while replacing said X ligand;

Z is selected from the group consisting of H, OR, NR₂, CR, CR₂, CR₃, SR, SiR₃, PR₂ and BR₂;

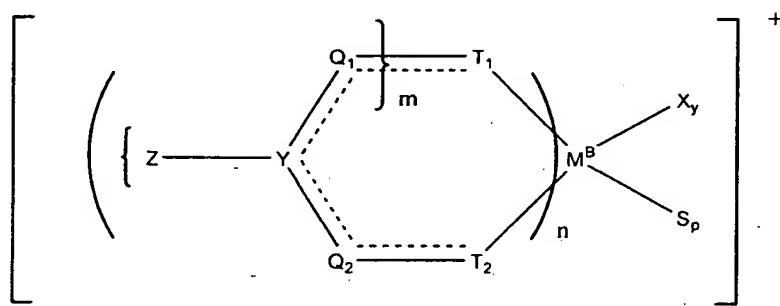
S is a solvent molecule;

n is 1, 2 or 3;

y equals (B-n-1); and

p is 0 or an integer to satisfy octahedral coordination requirements of the transition metal.

4. The process according to claim 1, wherein said cationic form of said octahedral transition metal complex has the formula:



wherein:

M is a transition metal atom selected from groups III, IV and V of the periodic table;

B is the valency of M and equals 3, 4 or 5;

Y is selected from the group consisting of C, N, S, P, B and Si;

X is an anionic ligand;

Q₁, Q₂, T₁ and T₂ are each independently selected from the group consisting of O, OR, N, NR, NR₂, CR, CR₂, S, SR, SiR₂, B, BR, BR₂, P, PR and PR₂, where each R is independently H or a group containing C, Si, N, O, B and/or P, whereas one or more R groups may be attached to said transition

metal atom M while replacing said X ligand;

Z is selected from the group consisting of H, OR, NR₂, CR, CR₂, CR₃, SR, SiR₃, PR₂ and BR₂;

S is a solvent molecule;

n is 1, 2 or 3;

y equals (B-n-1);

m is 1, 2, 3 or 4

p is 0 or an integer to satisfy octahedral coordination requirements of the transition metal.

5. The process according to claim 1, wherein said octahedral transition metal complex is of a symmetry selected from the group consisting of C₂ and C₃ symmetries, said transition metal is selected from the group consisting of zirconium and hafnium, said adjusting pressure consists of applying high pressures, and wherein substantially pure isotactic poly alpha-olefins are produced.

6. The process according to claim 1, wherein said octahedral transition metal complex is of a symmetry selected from the group of C₂ and C₃ symmetries, said transition metal is selected from the group consisting of zirconium and hafnium, said adjusting pressure includes alternating pressure between high pressure and low pressure, and wherein elastomeric poly alpha-

olefins are produced.

7. The process according to claim 6, wherein said alternating pressure is carried out at a frequency about equal to or lower than the polymerization insertion rate.

8. The process according to claim 6, wherein said alternating pressure is carried out at a frequency of about 10^{-4} to 100 Hertz.

9. A process for the polymerization of one or more alpha-olefins having at least 3 carbon atoms, comprising contacting alpha-olefin monomer or monomers in a solvent selected from the group consisting of polar solvents and non-polar solvents under polymerization conditions and above atmospheric pressure with a homogeneous catalyst system, said homogeneous catalyst system including:

- (i) a cationic form of a chiral or a non chiral octahedral titanium complex, comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands; and
- (ii) an anion of an acid selected from the group consisting of a Lewis acid and a Brønsted acid, to obtain an elastomer.

10. The process according to claim 9, wherein said homogeneous catalyst system includes a racemic or non-racemic mixture of said chiral octahedral titanium complex.

11. A process for the polymerization of one or more alpha-olefins having at least 3 carbon atoms, comprising contacting alpha-olefin monomer or monomers in a solvent selected from the group consisting of polar solvents and non-polar solvents under polymerization conditions, at or above atmospheric pressure, with a homogeneous catalyst system, said homogeneous catalyst system including:

- (i) a cationic form of an octahedral titanium complex having C_s symmetry; and
- (ii) an anion of an acid selected from the group consisting of a Lewis acid and a Brønsted acid, to obtain an elastomer.

12. The process according to claim 1, wherein said octahedral transition metal complex has C_1 symmetry and comprises one bidentate chelating ligand, said transition metal is selected from the group consisting of zirconium and hafnium, said adjusting the pressure consists of applying high pressures, and wherein the poly alpha-olefins produced are substantially elastomeric.

13. The process according to claim 3 or 4, wherein said octahedral transition metal complex has C_1 symmetry, n equals one, said transition metal is selected from the group consisting of zirconium and hafnium, and wherein high pressure is applied to produce poly alpha-olefins that are substantially elastomeric.

14. The process according to any one of claims 1, 5, 6 or 7, wherein said transition metal is selected from the group consisting of vanadium, niobium, tantalum, scandium, yttrium, lanthanum, lanthanides, and actinides.

15. A homogeneous catalyst system for the polymerization of alpha-olefins, said homogeneous catalyst system comprising:

- (a) a cationic form of a chiral octahedral transition metal complex comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands and having symmetry selected from the group consisting of C_1 , C_2 and C_3 symmetries; and
- (b) an anion of an acid selected from the group consisting of a Lewis acid and a Brønsted acid.

16. The homogeneous catalyst system of claim 15, wherein said symmetry is C_1 symmetry.

17. The homogeneous catalyst system of claim 15, wherein said symmetry is C_2 symmetry.

18. The homogeneous catalyst system of claim 15, wherein said symmetry is C_3 symmetry.

19. A homogeneous catalyst system comprising a cationic form of an octahedral titanium complex having C_s symmetry, and an anion of an acid selected from the group consisting of a Lewis acid and a Brønsted acid.

20. A polymerization process comprising the steps of contacting styrene monomer or monomers comprising styrene in a solvent selected from the group consisting of polar and non-polar solvents under polymerization conditions and at a pressure of about atmospheric or higher with a homogeneous catalyst system including:

- (i) a cationic form of a chiral octahedral transition metal complex comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands and having symmetry selected from the group consisting of C_1 and C_2 symmetries; and
- (ii) an anion of an acid selected from the group consisting of a Lewis acid and a Brønsted acid;

to obtain syndiotactic polystyrene or a copolymer comprising syndiotactic

polystyrene.

21. The process according to claim 20, wherein said homogeneous catalyst system has an activity exceeding about 2.5×10^6 gram polymer per mole catalyst per hour and wherein the said syndiotactic polystyrene has a stereoregularity exceeding about 99.9%.

22. The process according to claim 20, wherein said monomers comprising styrene include aliphatic alpha-olefin, and wherein said polymerization conditions include operation at low pressure, such that an elastomeric copolymer containing sequences of syndiotactic polystyrene and atactic poly-aliphatic alpha-olefins is obtained.

23. The process according to claim 22, wherein said aliphatic alpha-olefin is propylene.

24. The process according to claim 20, wherein said monomers comprising styrene include aliphatic alpha-olefin, and wherein said polymerization conditions include operation at alternating pressure, such that an elastomeric copolymer containing sequences of syndiotactic polystyrene and elastomeric poly-aliphatic alpha-olefins is obtained.

25. The process according to claim 24, wherein said aliphatic alpha-olefin is propylene.

26. A catalyst for the hydrogenation of olefins comprising an octahedral transition metal complex selected from the group consisting of C_2 -symmetry or C_3 -symmetry complexes, monoheteroallylic complexes, and combinations thereof.

27. The process according to claim 9, wherein said monomer comprises propylene, or wherein said poly alpha-olefins produced include polypropylene.

28. A process for the polymerization of one or more alpha-olefins having at least 3 carbon atoms, the process comprising the step of contacting alpha-olefin monomer or monomers in a solvent selected from the group consisting of polar solvents and non-polar solvents under polymerization conditions, at or above atmospheric pressure, with

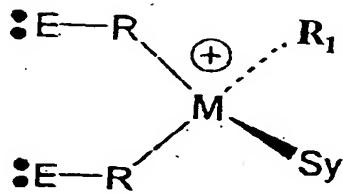
(i) a homogeneous catalyst system, said homogeneous catalyst system comprising a cationic form of a tetrahedral complex having a transition metal center, and one or more Lewis basic pendant groups, said pendant groups being capable of donating one or more pairs of free electrons to said transition metal center;

and

(ii) an anion of an acid selected from the group consisting of a Lewis acid and a Brønsted acid;

to obtain an elastomer having a particular degree of stereoregularity.

29. The process according to claim 28, wherein said cationic form of said tetrahedral complex is of the form:



wherein:

E is a donating group with a free pair of electrons;

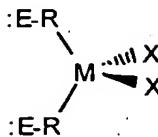
R₁ is selected from the group consisting of H, alkyl, aryl and silyl;

S is a solvent molecule;

y is 0 or 1; and

R is C, B, N, P, O, S or any other anionic bridging group.

30. The process according to claim 28, wherein said tetrahedral complex is of the form:



wherein:

X is a halide;

E is a donating group with a free pair of electrons; and

R is C, B, N, P, O, S or any other anionic bridging group.

31. The process according to claim 28, wherein said cationic form of said tetrahedral complex is converted through dynamic equilibrium to a cationic octahedral complex.

32. The process according to claim 28, wherein a combination of a specific cationic form of a tetrahedral complex, specific monomer or monomers, specific solvent, and specific polymerization conditions are employed so as to tailor said degree of stereoregularity of said elastomer.

33. The process according to claim 1, wherein said octahedral transition metal complex is of a symmetry selected from the group of C₂ and C₃

symmetries, said transition metal is selected from the group consisting of zirconium and hafnium, said adjusting pressure consists of operating at high pressure to produce stereoregular poly alpha-olefins and operating at low pressure in the presence of said stereoregular poly alpha-olefins to produce atactic poly alpha-olefins that are incorporated into said stereoregular poly alpha-olefins, thereby producing an elastomeric polymer or copolymer.

34. The process according to claim 33, wherein said elastomeric polymer or copolymer includes polypropylene.

1/3

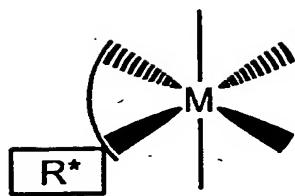


Fig. 1a

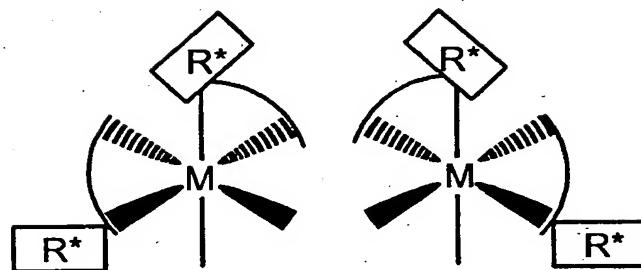


Fig. 1b

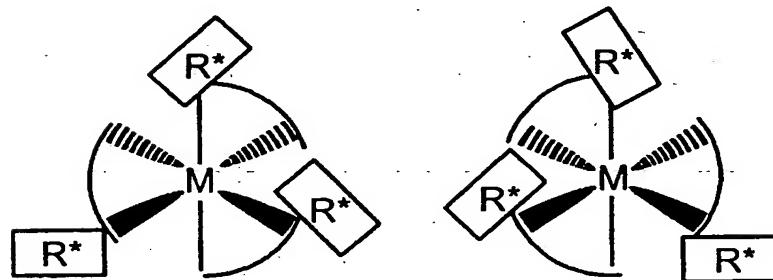


Fig. 1c

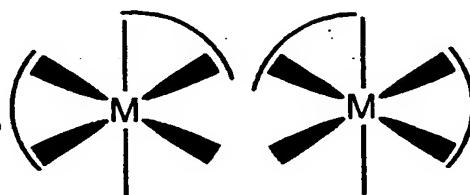
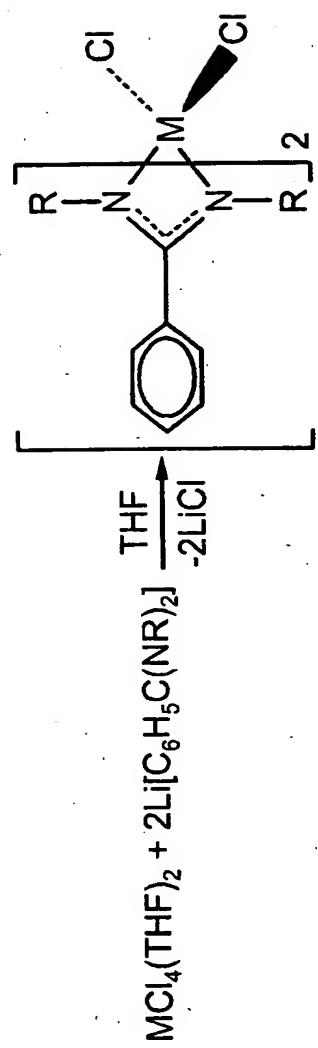


Fig. 2



1:M = Ti, R = i-Pr
 2:M = Zr, R = i-Pr
 3:M = Ti, R = Cy
 4:M = Zr, R = Cy

Fig. 3

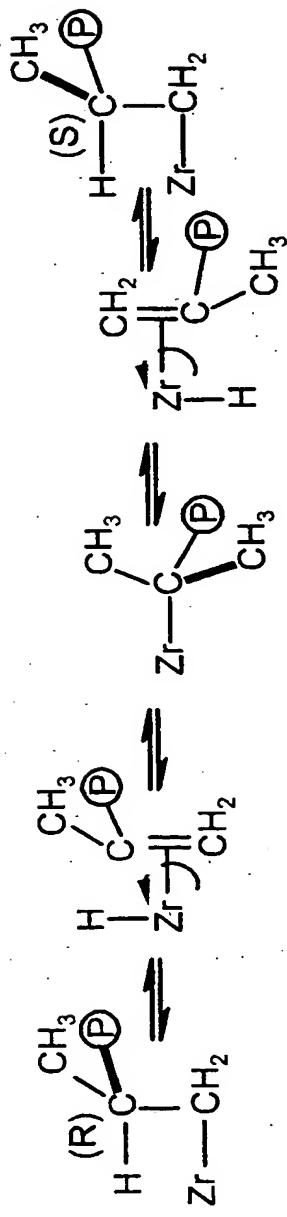
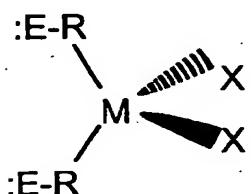
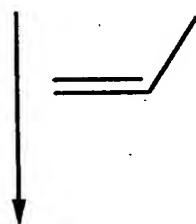
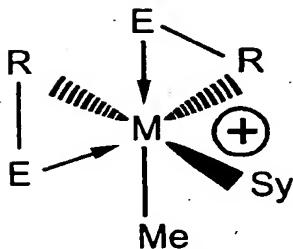
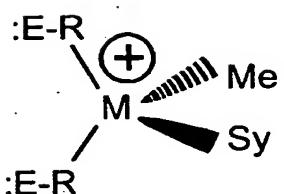
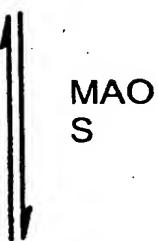
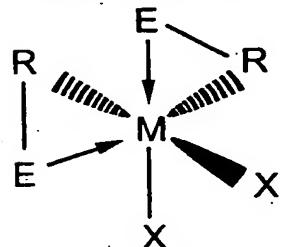


Fig. 4

Tetrahedral Complex



Octahedral Complex



atactic polypropylene

Isotactic polypropylene

Fig. 5

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
2 August 2001 (02.08.2001)

PCT

(10) International Publication Number
WO 01/55227 A3(51) International Patent Classification⁷: C08F 4/16, 4/38, B01J 31/18, 31/22, 31/38

(74) Agent: G. E. EHRLICH (1995) LTD.; 28 Bezalel Street, 52 521 Ramat Gan (IL).

(21) International Application Number: PCT/IL01/00073

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(22) International Filing Date: 25 January 2001 (25.01.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/492,033. 27 January 2000 (27.01.2000) US

(71) Applicant (for all designated States except US): TECHNION RESEARCH AND DEVELOPMENT FOUNDATION LTD. [IL/IL]; Gutwirth Science Park, Technion City, 32 000 Haifa (IL).

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

(75) Inventors/Applicants (for US only): EISEN, Moris [IL/IL]; 68 Hashkedim Street, 34 601 Tivon (IL). VOLKIS, Victoria [IL/IL]; Neve Sha'anana, 61 Netivey Chen Street, 32 688 Haifa (IL). SHMULINSON, Michael [IL/IL]; Ramat Almogi, 9 Hasachlav Street, 34 790 Haifa (IL). AVERBUIJ, Claudia [IL/IL]; 1 Einav Street, 21 970 Carmiel (IL). TISH, Edith [IL/IL]; 16 Arie Street, 78 701 Ashkelon (IL).

Published:

— with international search report

(88) Date of publication of the international search report:
31 January 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 01/55227 A3

(54) Title: PROCESS FOR THE PRODUCTION OF STEREOREGULAR POLYMERS AND ELASTOMERS OF ALPHAOLEFINS AND CERTAIN NOVEL CATALYSTS THEREFOR

(57) Abstract: A process for the polymerization of one or more alpha-olefins having at least 3 carbon atoms, which comprises contacting the monomer or monomers in a polar or non-polar solvent under polymerization conditions with a homogeneous catalyst system including (a) a cationic form of a racemic mixture of a chiral octahedral transition metal complex or of a non chiral octahedral transition metal complex, comprising 1, 2 or 3 bidentate chelating ligands and no cyclopentadienyl ligands and having C₁, C₂, or C₃ symmetry; and (b) an anion of a Lewis acid or a Brönsted acid; and adjusting the pressure so as to obtain either a highly stereoregular polymer or copolymer or an elastomer.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/IL01/00073

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08F 4/16, 4/38; B01J 31/18, 31/22, 31/38

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/104, 155, 162, 167; 526/126, 161, 172, 348.6; 556/10, 13, 38, 51

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Non-Patent Literature Search, American Chemical Society and Chem Connect

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,A	US 5,707,913 A (SCHLUND et al) 13 January 1998 col. 1, line 5 through col. 5, line 50.	1-34
X,A	US 6,013,745 A (MCKAY et al) 11 January 2000, col. 1, line 5 through col. 7, line 38.	1-34
X,A	US 5,318,935 A (CANICH et al) 07 June 1994, col. 1, line 10 through col. 10, line 47.	1-34
X,A	EP 0 675 138 A1 (YOKOTA) 04 October 1995, pages 2-17.	1-34
X,A	VOLKIS et al Organometallics 1998, vol. 17, No. 15, pages 3155-3157.	1-34
X,A	FLORES et al Organometallics 1995 Vol. 14, No. 4, pages 1827-1833.	1-34

 Further documents are listed in the continuation of Box C. See patent family annex.

•	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

23 APRIL 2001

Date of mailing of the international search report

08 MAY 2001

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 872-9559

Authorized officer

ROBERT D. HARLAN

Jean Proctor
Paralegal Specialist

Telephone No. (703) 306-5926

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IL01/00073

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,A	HERSKOVICES-KORINE et al Journal of Organometallic Chemistry 1995, Vol. 503, pages 307-314.	1-34
X,A	SCOLLARD et al Marcomolecules 1996, Vol. 29, No. 15, pages 5241-5243.	1-34
X,A	MACK et al Journal of Organometallic Chemistry 1996, Vol. 525, pages 81-87.	1-34
X,A	AVERBUJ et al Journal of American Chemical Society 1998, Vol. 120, No. 14, pages 8640-8646.	1-34

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IL01/00073

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

502/104, 155, 162, 167; 526/126, 161, 172, 348.6; 556/10, 13, 38, 51

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.